PYROLYSIS OF UTAH TAR SANDS--PRODUCTS AND KINETICS

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INTRODUCTION

Bitumen-impregnated sandstone, or tar sand, represents an enormous world hydrocarbon source, estimated at over one trillion barrels of oil in place. Although the vast majority of this resource is found in the deposits of western Canada and eastern Venezuela, sizeable portions, currently estimated at 30 billion barrels, reside in the continental U.S.; most of this is located in the state of Utah. A small percentage of this world resource is recoverable by known or projected surface mining methods. The bulk can be recovered only by the development of effective and economical in situ recovery methods which allow the recovery of oil values from in-place deposits without the need of extensive mining operations.

Many methods have been proposed for the in situ recovery of unaltered and/or modified bitumen from tar sand deposits (1). Of these, in situ thermal methods possess many attractive features over other proposed in situ recovery methods. In general, thermal recovery refers to the process of in-place heating of the tar sand, usually through combustion of a portion of the tar sand bitumen, allowing recovery of bitumen as a now-mobile tar or as a cracked bitumen product. It is this process of in-place thermal cracking that is of particular interest to us and which prompted this study of the pyrolytic behavior of tar sands as a part of the Laramie Energy Research Center's overall effort in the development of in situ tar sand recovery technology.

Studies of the thermal cracking of petroleum materials have been extensive (2); however, studies directed at the thermal cracking of tar sand bitumen have been only sparsely reported (3). Most of these latter studies investigated the cracking properties of bitumen after it had been separated from the accompanying sand. Conclusions drawn from pyrolysis studies of separated bitumen may not be valid when applied to pyrolysis of bitumen that remains in contact with mineral material as in the natural state. Rather, one would expect to find differences in the product yields and observed kinetics from pyrolysis of neat bitumen vs pyrolysis of bitumen-sand because of such system differences as thermal conductivity, product escape paths, surface area to bulk volume ratios, and mineral catalysis.

This paper reports a laboratory study of the thermal cracking behavior of four Utah tar sands and a Canadian tar sand in which no prior separation of bitumen from the mineral material has taken place. This thermal cracking behavior has been investigated in terms of the products formed, i.e., liquid products, gaseous products, and char. The kinetics of the overall pyrolysis reaction has been suggested.

EXPERIMENTAL

Tar Sand Samples

Representative samples of the parent tar sand material listed below were frozen in liquid nitrogen and crushed to pass a 14-mesh (U.S. series No. 16) screen. This sized material was used in all pyrolysis experiments.

Northwest Asphalt Ridge tar sand from a core of the 295- to 305-ft zone at NW1/4 NE1/4 SE1/4 sec. 23, T. 4 S., R. 20 E., Uintah Co., Utah;

P.R. Spring tar sand outcrop material from NE sec. 32, T. 15-1/2 S., R. 23 E., Uintah Co., Utah;

Tar Sand Triangle tar sand from a core of the 1180- to 1200-ft zone at SW1/4 SE1/4, sec. 22, T. 30 S., R. 16 E., Wayne Co., Utah;

Sunnyside tar sand from a core of the 421- to 438-ft zone at NE1/4 SW1/4, sec. 31, T. 13 S., R. 15 E., Carbon Co., Utah;

Athabasca tar sand from a pit-run sample supplied by the Great Canadian Oil Sands Co., Alberta, Canada.

Pyrolysis Experiments

Product Collection Experiments. - Pyrolysis experiments were performed using a horizontal tube furnace, equipped with an electronic temperature controller, to heat a 250-mm section of pyrex pyrolysis tube (20-mm i.d.) containing charges of 140 to 170 g of tar sand. Heat-up rates were such that the desired temperatures (500, 750, and 1000°F) were reached within 15 min. All experiments were conducted under a nitrogen atmosphere flowing at 0.5 l/min (uncorr.) corresponding to a flux rate of 230 scf/ft^2/hr. The nitrogen was preheated to approximate final furnace temperature. Major liquid products were collected in two receivers; the first was an air condenser, the second was an ice-cooled trap. In all runs the majority of products were collected at the air condenser; only trace amounts of very light products were collected in the ice trap. All oil products were combined, sealed, and stored under nitrogen at 5°F for later analysis. Gas samples were collected in 100-ml gas sampling bottles downstream of the ice trap.

Product Analysis. - Oil products were analyzed for elemental composition, specific gravity (60°F/60°F), and Ramsbottom carbon residue. Oil products were analyzed for saturates, aromatics, polar aromatics, and asphaltenes (SAPA analysis). This involves deasphaltening with n-pentane and chromatography of the resulting maltenes on a water-jacketed column containing 200 g of grade 62 silica gel (Grace) made up in n-pentane (loading ratio 100:1); successive elution with n-pentane, benzene, and benzene/methanol (9:1) separated the maltenes into saturate, aromatic, and polar aromatic fractions, respectively. Simulated distillation analyses of the oil products were obtained by the internal standard method of Poulson, et al. (4). Gas analyses were obtained using a CEC-21-620 mass spectrometer.

Kinetic Experiments

Kinetic data were obtained using the same tube furnace with its preheated, inert sweep-gas arrangement (flow rate 0.2 l/min, uncorr, flux rate 92 scf/ft^2/hr); however, the pyrolysis tube was modified to allow the ready insertion and removal of small ceramic combustion boats containing the tar sand samples. Prior to a run, the furnace temperature was adjusted to the desired temperature, using a thermocouple contained within a boat filled with 6.5 g of clean sand. Once thermally established, the furnace showed a maximum drift of ± 2°F over a 3-hr period. Runs were performed by inserting into the hot zone of the pyrolysis tube an accurately weighed sample of approximately 6.5 g of tar sand contained in a ceramic boat. The boat was placed in the hot zone for the desired time period, drawn to the cold end of the tube, and cooled for 2 min under a nitrogen atmosphere. The boat was then removed, rapidly cooled in powdered dry ice, and stored in a dessicator. Upon returning to ambient temperature, the boat was weighed to record the total volatile loss and placed in a glass extraction thimble containing a fine fritted disc overlaid with a glass-fiber pad. The thimble was weighed and extracted exhaustively with hot benzene/ethanol, 3/1, in a modified Soxhlet extractor (5). After extraction, the thimble and boat were dried in vacuo at 175°F and reweighed; the difference in initial and final weights was taken as the weight of extractable bitumen remaining on the tar sand.

RESULTS AND DISCUSSION

Pyrolysis Products

Although the chemical processes occurring in tar sands bitumen at elevated temperatures are most likely numerous and complex, the overall conversion can be viewed simply as given in Equation 1:

$$\text{Bitumen} \xrightarrow{k_B} \text{Oil} + \text{Gas} + \text{Coke} \qquad 1)$$

that is, that bitumen upon heating is converted into three products; oil, gas, and coke. To be useful, this view requires a definition of terms. Bitumen is the total native organic portion of tar sand that is soluble in boiling benzene/ethanol; oil is the sum of all liquid products, condensable at 0°C, that volatilizes from the heated tar sand material; gas is the total volatile product, not condensable at 0°C, that is evolved from the heated tar sand; and coke is the benzene/ethanol-insoluble, nonvolatile carbonaceous material remaining on the sand after bitumen decomposition. Implicit in this definition is the realization that native bitumen may contain material defined as oil and gas before pyrolysis.

Pyrolysis experiments were performed on the four Utah and one Canadian tar sands at 500, 750, and 1000°F under a flowing, inert atmosphere. Analyses of starting bitumens, oil recovery, and routine product inspections of the pyrolysis oils are given in Table 1. Several general trends are apparent in these data. Oil recovery increased with increasing temperature, although the majority of this increase occurred as the temperature was increased through the lower pyrolysis temperatures, i.e., 500 to 750°F. At temperatures from 750 to 1000°F, oil recoveries increased only moderately with the increased temperature. Oil recoveries represent actual oil product collected and do not account for the possible loss of oil due to mist formation. Coke-forming character of the bitumens generally followed their Ramsbottom carbon residue values except for the P.R. Spring sample which showed a very low coking value. Coke values at 500°F are not reported, as the pyrolysis was very incomplete at this temperature leaving large quantities of extractable bitumen and essentially no coke. Elemental analyses of the produced oils indicated that pyrolysis caused little change in the C/H ratio while affecting a reduction in nitrogen and sulfur content. As compared to the parent bitumen, specific gravities of the produced oils decreased throughout the pyrolysis temperature range while Ramsbottom carbon residue values dropped on all produced oils. Pour points of the produced oils were low for the 500°F pyrolysis and increased for the 750 and 1000°F oils. Pour points for the Asphalt Ridge 750 and 1000°F pyrolysis oils were unusually high, perhaps reflecting the presence of heavy hydrocarbons in these oils as further evidenced by their waxy appearance.

The produced oils and the starting bitumens were analyzed by silica gel chromatography to determine their major compositional fractions. They were deasphaltened with n-pentane and the resulting maltenes chromatographed on silica gel to give saturates, aromatics, and polar aromatics fractions. The results of this chromatographic analysis (SAPA) are given in Table 2. All produced oils contained a substantially higher saturates content than the parent bitumen and essentially no asphaltenes. As the pyrolysis temperature is increased there is a clear shift in the SAPA fractions toward the more polar constituents. At lower temperatures, the polar constituents, both native and cracked products, probably lack sufficient volatility to escape the bitumen, and remain behind to be further cracked until they are sufficiently volatile to escape. As the pyrolysis temperature is increased, these polar materials are capable of vaporizing from the bitumen in a molecular state retaining their polar character.

Simulated distillation analysis of the tar sand bitumens and of the produced pyrolysis oils from these bitumens is given in Table 3. The data are reported as the weight percent of the sample distilling within 100° ranges from 300° to 1000°F. Material distilling above 1000°F is classified as residuum. Because the sample oils were analyzed in benzene solution, this analysis did not allow accurate determination of materials distilling between 0° and 300°F; however, qualitative inspection of the corresponding GC traces indicated that the quantity of material distilling in this range is small, estimated to be 0 to 2 wt percent.

Although minor differences may be observed among the distilling range characteristics of the various produced oils reported in Table 3, more significant are the similarities. All tar sands, regardless of pyrolysis temperature, produced only small amounts, usually 10 percent or less of oil boiling under 500°F. However, the distillation curves for all produced oils showed the same trend toward higher proportions of the product distilling at higher temperatures as the pyrolysis temperature increased. An important observation can be made considering the distillation data and the oil recovery data (Table 3 and Table 1). At a pyrolysis temperature of 750°F, oil recovery is high, approaching that attainable at 1000°F, while the distillation character of the 750°F product oil indicates this material is considerably lighter than that produced at 1000°F. That is, a lower boiling product oil can be generated at the lower pyrolysis temperature with a moderate reduction in oil recovery or increase in coke formation.

Results of the analyses of the gases produced during the pyrolysis are given in Table 4. Although it was not possible in these experiments to obtain an accurate material balance on the gases produced, due to misting of the oil, incomplete bitumen conversion, and dilution with inert gas, the reported values represent the composition of the gas (nitrogen-free) averaged over the entire pyrolysis. The produced gas was predominantly composed of hydrogen and methane, with C_2 and C_4 hydrocarbons being next most abundant. Also produced were small quantities of other gases such as carbon dioxide, carbon monoxide, carbonyl sulfide, and hydrocarbons above C_5. Production of hydrogen sulfide was high for Athabasca tar sands, which contains high-sulfur bitumen, but low for Tar Sand Triangle tar sands, which also contains high-sulfur bitumen. This difference suggests that the sulfur in these tar sands is incorporated into chemically different species, thereby significantly affecting the production of hydrogen sulfide from the two bitumens.

Pyrolysis Kinetics

The overall reaction depicted in Equation 1 defines the pyrolysis process as one involving the conversion of bitumen (reactants) to oil, gas, and coke (products) by the application of heat to a tar sand. Many chemical and physical processes contribute to this conversion and to the observed loss of bitumen, each process being governed by its own concentration and rate dependencies. The overall rate constant, k_B, describing this process is therefore a net rate constant, being the summation of all contributing processes. Although the pyrolysis is complex, two basic steps encompass the net conversion: 1) cracking of low-volatility organics to yield products of higher volatility and coke and 2) vaporization of the native and produced oils allowing their escape from the bitumen-sand matrix. It is not possible from the present study to separate these steps to study their kinetics independently thereby obtaining true rate data in the fundamental sense. Rather our approach has been to study the rate of loss of bitumen in a process sense where the determined rate data reflect not only cracking and product volatilization rates, but also other contributing experimental variables such as bitumen film thickness, sample porosity, inert atmosphere sweep rates, and others.

Analysis of our data to determine reaction order indicated that the best straight-line fit was obtained by application of a first-order treatment to the loss of bitumen as a function of time. The first-order rate equation expressing this relation is given in Equation 2 (6, 7):

$$k_B = \frac{1}{t} \ln [a_0/(a_0-x)] \qquad 2)$$

where: t = reaction time
a_0 = initial quantity of bitumen
x = quantity of bitumen disappearing in time (t)

Figure 1 is the plot of data obtained for the pyrolysis of the Asphalt Ridge tar sand at four temperatures plotting time (t) vs $\ln [a_0/(a_0-x)]$. These plots show that temperatures of 800, 900, and 1000°F produce good straight lines after the initial heat-up period, whereas the 700°F run resulted in a nonlinear plot throughout the entire time span. Analysis of the data for pyrolysis of the other tar sand samples gave plots of very similar character to Figure 1 with only minor differences in line position at the specific pyrolysis temperatures.

Rate constants, k_B, for each of these pyrolyses were determined from the slope of plots of Equation 2, using the best fitting linear regression line. Statistical coefficients of determination for these regression lines were 0.96-0.99 for the 800, 900, and 1000°F runs, indicating a good to excellent straight line fit, while that for the 700°F runs were 0.90 to 0.92, indicating nonlinearity and/or significant curvature in the data points.

The rate constants calculated for the five tar sands are given in Table 5. The pyrolysis rates increased by a factor of about 200 as pyrolysis temperatures increased from 700° to 1000°F. Bitumen half-life values, $t_{1/2}$, were calculated from the observed rate constants and are given in Table 5. These $t_{1/2}$ values ranged from 5800 to 8500 sec at 700°F to 37 to 63 sec at 1000°F.

An Arrhenius (6) plot (1/T vs $\ln k_B$) for the P. R. Spring tar sand pyrolysis is shown in Figure 2. Similar plots for the other four sets of rate constants allowed the calculation of apparent Arrhenius activation energies, given in Table 5, for the pyrolysis of each tar sand. Straight line correlations were obtained for each Arrhenius plot, with coefficients of determination of 0.94 to 0.99. The apparent Arrhenius activation energies for the pyrolysis of the five tar sands were nearly equal, which suggests that the pyrolysis steps contributing to the rate-determining process are similar in each case; and although the rate constants at a given temperature vary from tar sand to tar sand, the effect of an increase in temperature on the reaction rate is the same in each.

SUMMARY

The general pyrolytic behavior of the Utah tar sands is remarkably similar deposit to deposit and follows the trends in pyrolysis characteristics of the Athabasca tar sands. Common to all tar sands investigated is the production by pyrolysis of an upgraded oil, relative to the native bitumen, in terms of elemental composition, SAPA composition, distillate content, carbon residue, and specific gravity. The rate constants for bitumen pyrolysis, measured as the rate of loss of extractable bitumen, were found to be first order in bitumen and to range from 1×10^{-4} sec^{-1} at 700°F to 200×10^{-4} sec^{-1} at 1000°F. Each tar sand pyrolysis exhibited an apparent Arrhenius activation energy in the range of 33 to 35 kcal, suggesting a similarity between the tar sands in their principle pyrolysis processes.

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TABLE 1. - Analysis of tar sand bitumens and pyrolysis oils

Tar sand	Pyrolysis temp, °F	Oil recovery, wt. % of starting bitumen	Coke formed, wt. % of bitumen	C	H	N	S	C/H	Rams-bottom carbon	Specific gravity, 60/60	Pour points, °F
Asphalt Ridge	Bitumen			86.74	13.04	1.06	0.77	0.55	7.76	0.963	95
	500	17	--	86.26	12.08	0.31	0.41	0.59	nil	0.923	-40
	750	72	7	85.88	11.98	0.56	0.36	0.60	nil	0.906	115
	1000	86	7	85.96	11.86	0.76	0.40	0.60	0.90	0.932	160
P.R. Spring	Bitumen			86.51	10.77	1.31	0.56	0.67	12.49	1.006	115
	500	19	--	86.34	11.75	0.33	0.46	0.61	nil	0.936	-5
	750	75	4	86.05	11.68	0.87	0.41	0.61	1.12	0.952	40
	1000	84	2	85.39	11.20	0.96	0.54	0.63	3.78	0.953	40
Tar Sand Triangle	Bitumen			84.62	10.41	0.55	4.49	0.68	20.26	1.020	95
	500	20	--	85.13	12.04	0.06	2.55	0.59	0.85	0.951	5
	750	45	26	85.63	11.65	0.15	2.82	0.61	1.40	0.935	30
	1000	56	25	85.85	10.97	0.25	3.09	0.65	3.38	0.953	25
Sunnyside	Bitumen			84.05	11.58	0.95	0.44	0.60	15.17	0.980	115
	500	14	--	86.72	12.19	0.29	0.32	0.59	nil	0.931	-30
	750	55	16	86.65	12.05	0.71	0.18	0.60	1.94	0.958	15
	1000	68	12	86.67	11.94	0.66	0.31	0.60	3.46	0.964	60
Athabasca	Bitumen			81.66	11.23	0.44	4.71	0.61	12.63	1.006	70
	500	23	--	84.67	11.68	0.06	2.28	0.60	1.60	0.919	-50
	750	59	12	84.18	11.21	0.14	3.09	0.63	1.81	0.927	-15
	1000	75	12	84.12	11.09	0.20	3.48	0.63	3.38	0.945	-15

TABLE 2. - SAPA analysis of tar sand bitumens and pyrolysis oils

Tar sand	Pyrolysis temp, °F	Saturates, wt. %	Aromatics, wt. %	Polar aromatics, wt. %	Asphaltenes, wt. %
Asphalt Ridge	Bitumen	48	18	27	6
	500	90	6	4	0
	750	84	11	6	0
	1000	77	13	9	1
P.R. Spring	Bitumen	29	25	35	11
	500	82	8	10	0
	750	74	16	12	0
	1000	65	18	13	1
Tar Sand Triangle	Bitumen	42	22	10	26
	500	87	10	3	0
	750	91	7	2	0
	1000	70	25	5	0
Sunnyside	Bitumen	40	15	25	20
	500	83	7	10	0
	750	73	16	11	0
	1000	65	22	13	1
Athabasca	Bitumen	43	25	14	17
	500	95	3	2	0
	750	91	4	2	0
	1000	84	10	6	0

TABLE 3. - Simulated distillation analysis of tar sand bitumens and pyrolysis oils

Tar sand	Pyrolysis temp, °F	Wt. percent distillable in the range: °F							
		300-400	400-500	500-600	600-700	700-800	800-900	900-1000	Resid.
Asphalt Ridge	Bitumen	<1	2	3	4	6	12	16	56
	500	3	10	18	22	27	17	1	2
	750	2	6	9	11	15	24	22	11
	1000	4	7	9	10	13	19	19	19
P.R. Spring	Bitumen	<1	1	3	5	6	9	9	67
	500	2	12	23	30	22	7	1	2
	750	2	6	9	12	17	23	20	12
	1000	2	5	8	12	14	18	14	27
Tar Sand Triangle	Bitumen	<1	1	5	8	9	10	8	60
	500	<1	5	16	22	24	23	8	2
	750	2	5	13	17	20	20	13	9
	1000	3	4	11	14	17	18	15	18
Sunnyside	Bitumen	<1	<1	3	5	6	10	7	68
	500	1	8	20	31	21	13	2	4
	750	2	6	9	14	18	27	17	7
	1000	3	5	7	12	15	22	16	20
Athabasca	Bitumen	<1	2	5	8	10	10	10	55
	500	7	10	17	31	27	3	1	4
	750	4	8	19	23	25	13	2	6
	1000	6	8	12	17	17	17	11	12

TABLE 4. - Gas analysis

Tar sand	Pyrolysis temp., °F	Composition, wt. %, nitrogen-free[a/]							
		H_2	CH_4	C_2	C_3	C_4	C_5	H_2S	Other
Asphalt Ridge	500	36	15	18	2	1	0	0	28
	750	25	25	9	6	18	3	7	7
	1000	30	21	8	6	12	6	6	11
P.R. Spring	500	25	13	13	4	2	0	27	16
	750	27	24	9	6	14	6	2	12
	1000	28	30	8	4	6	4	1	19
Tar Sand Triangle	500	5	38	24	7	0	0	0	26
	750	11	23	14	10	21	10	9	2
	1000	26	47	12	3	5	1	3	3
Sunnyside	500	30	23	21	0	0	0	0	26
	750	36	25	13	6	16	1	1	2
	1000	56	31	4	1	4	1	0	3
Athabasca	500	19	8	14	1	1	0	14	43
	750	10	22	12	9	13	8	21	5
	1000	19	36	11	8	7	4	12	3

[a/] Nitrogen averaged 90 to 99% of total gas

TABLE 5. - Rate constants and apparent Arrhenius activation energies for tar sand pyrolysis

Tar sand	Pyrolysis temp., °F	$k_B \times 10^4$, sec^{-1}	$t_{1/2}$, sec	Apparent E_a, kcal	Arrhenius constant
Asphalt Ridge	700	0.81	8500	33	16.5
	800	4.5	1500		
	900	89	78		
	1000	110	63		
P.R. Spring	700	1.1	6300	33	16.5
	800	6.7	1000		
	900	64	110		
	1000	180	38		
Tar Sand Triangle	700	1.2	5800	33	16.5
	800	7.2	960		
	900	52	130		
	1000	150	46		
Sunnyside	700	0.88	7800	35	17.9
	800	5.1	1400		
	900	99	70		
	1000	160	43		
Athabasca	700	1.1	6300	33	16.4
	800	7.1	970		
	900	59	120		
	1000	190	37		

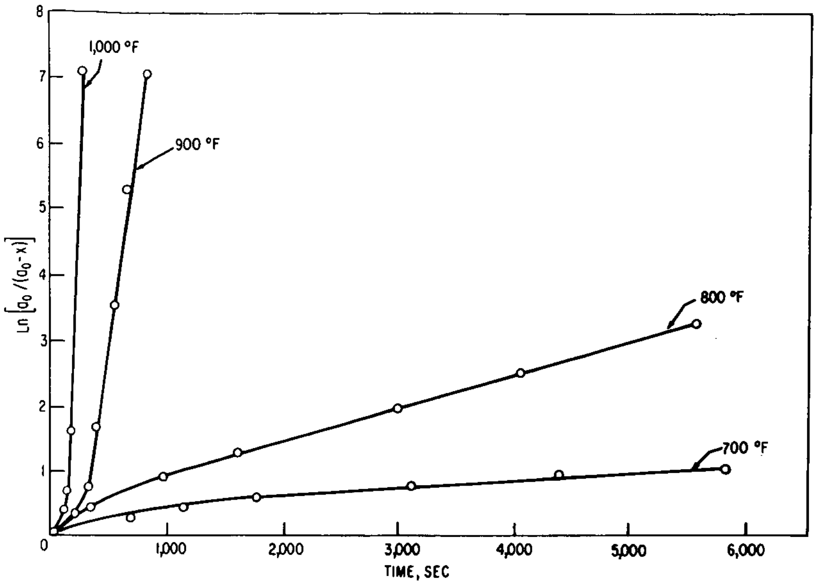

FIGURE 1.- FIRST-ORDER KINETIC PLOT FOR ASPHALT RIDGE TAR SAND PYROLYSIS.

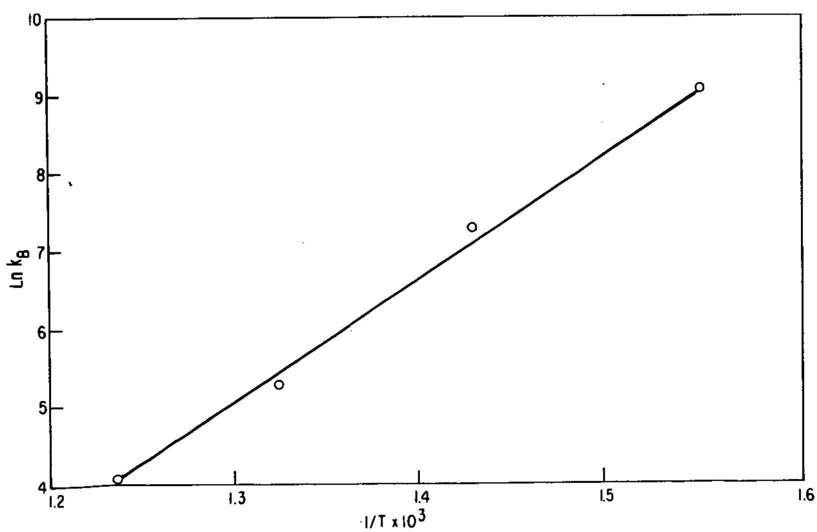

FIGURE 2.- ARRHENIUS PLOT FOR P.R. SPRING TAR SAND PYROLYSIS.